Preparation of β-$FeSi_2$ Films by Exchange Reaction Between Si Wafer and Molten Salts

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Materials for optical devices

- III-V and II-VI compound semiconductors
  - e.g. GaAs,CdSe

- Demerits
  - Harmful elements to human and environment
    - e.g. As,Cd
  - No adaptation to Si process

Fig. Various kinds of compound-semiconductors.

Reference HITACHI CABLE Homepage （http://www.densyou.co.jp/products/semiconductor/index.html）

What is β-$FeSi_2$

- Eco-friendly
  - Abundant on Earth
  - Harmless
- Semiconductor
  - Direct-bandgap (about 0.8eV)
  - Large light-absorption coefficient

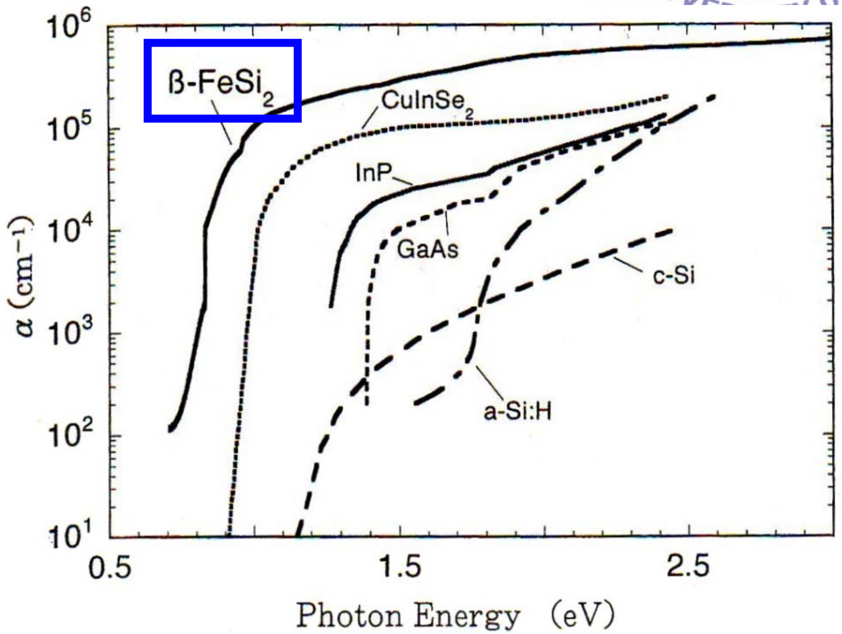


Fig. Absorption coefficient of various semiconductors.

Si-based devices application

- High efficiency photovoltaic cell
- Infrared Light Emitting Diode

Difficulty in forming β-$FeSi_2$ crystal

- β-$FeSi_2$ stable under 1210K
- To form β-$FeSi_2$ crystal
  - Solid phase reaction between ε-FeSi and α-$FeSi_2$
  - Supercooling over 230K

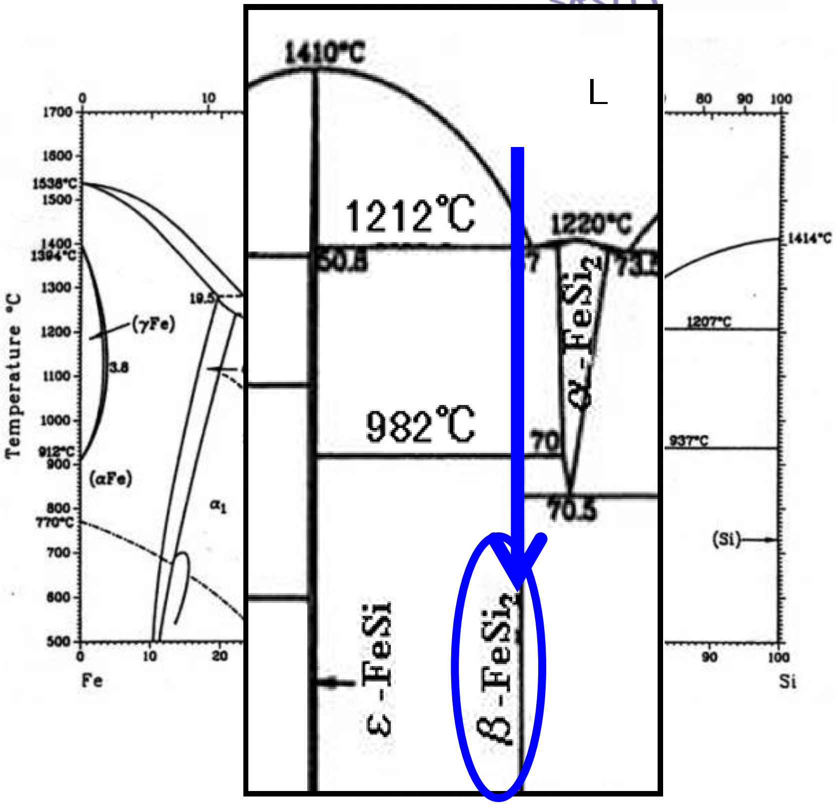


Fig. Phase diagram of Fe-Si binary system.

Impossible to form β-$FeSi_2$ directly from Fe-Si binary liquid

Previous Studies

Various formation methods

- Ion beam synthesis
- Multilayer method
- Chemical vapor deposition

etc.

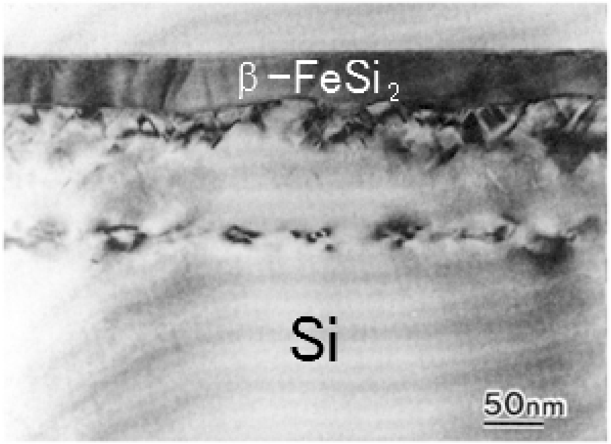


Fig. SEM image(up) of Sample by IBS method. Maeda *et al.*

Problem

- Slow deposition rate
- High energy (vacuum process)
- Unsuitable for mass production

Methodology in this work

Exchange reaction between Si and $FeCl_2$

Use Si wafer itself as raw material

$$5Si(s) + 2FeCl_2(l) = SiCl_4(g) + 2\beta\text{-}FeSi_2(s)$$

•By-product $SiCl_4$ is in gas phase and leaves molten salts
•Not interrupting the reaction

Controlling $FeCl_2$ vapor pressure

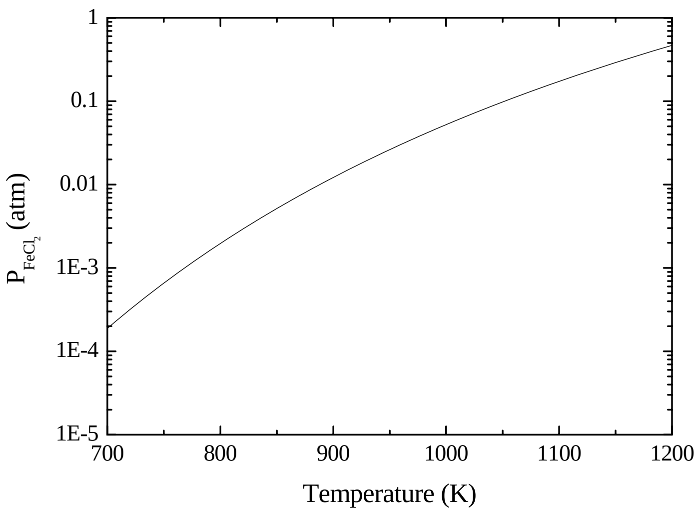


Fig. Vapor pressure of $FeCl_2$

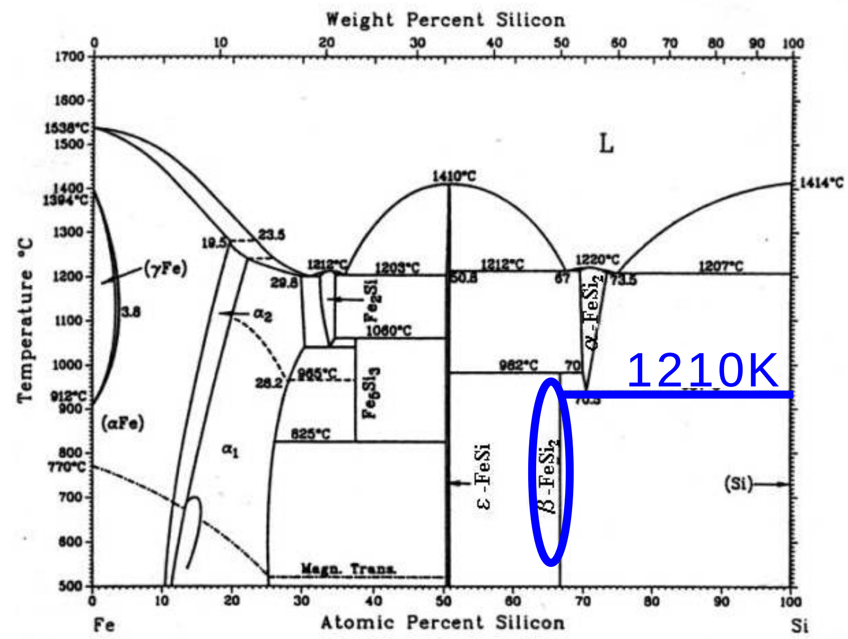


Fig. Phase diagram of Fe-Si binary system.

- Control $FeCl_2$ vapor pressure
- Formation of low melting point (<1210K) salts containing $FeCl_2$

NaCl-50at%KCl salts (m.p. 940K) containing $FeCl_2$

Controlling $FeCl_2$ vapor pressure

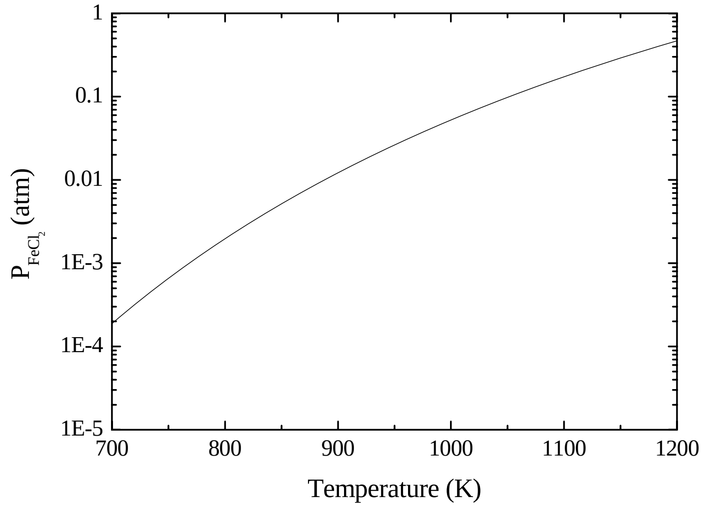


Fig. Vapor pressure of $FeCl_2$

- Control $FeCl_2$ vapor pressure
- Formation of low melting point (<1210K) salts containing $FeCl_2$

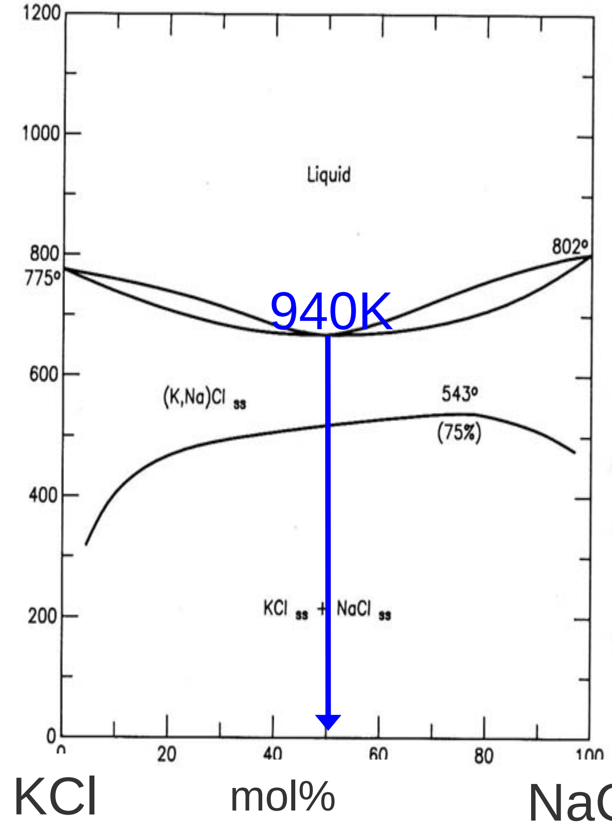


Fig. Phase diagram for KCl-NaCl system.

NaCl-50at%KCl salts (m.p. 940K) containing $FeCl_2$

Objective of this work

1. To confirm exchange reaction between Si and NaCl-KCl-$FeCl_2$ salts

2. To investigate the growth of β-$FeSi_2$ layer by the reaction

Experimental Procedure 1

Formation Step

- Si wafer
- NaCl-KCl-$FeCl_2$ Molten Salt

Ti powder

Quartz tube

- Evacuation by rotary pump
- He flow

Electric resistance furnace(1173K)

SEM and XRD measurement

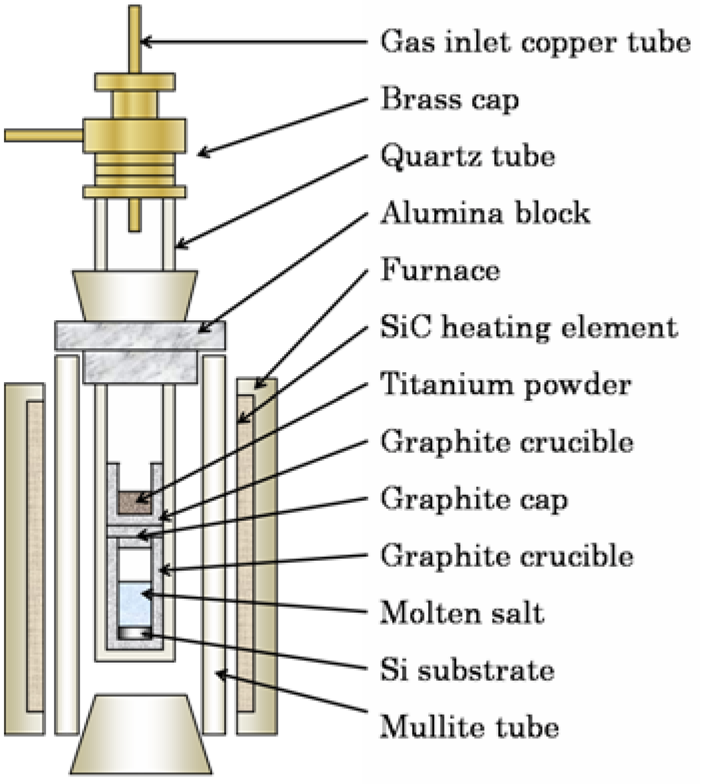


Fig. Schematic image of apparatus

Experimental Procedure 2

Annealing Step

Prepared Sample

Quartz tube

- Evacuation by rotary pump
- He flow

Electric resistance furnace
(1173K 12hours)

SEM and XRD measurement

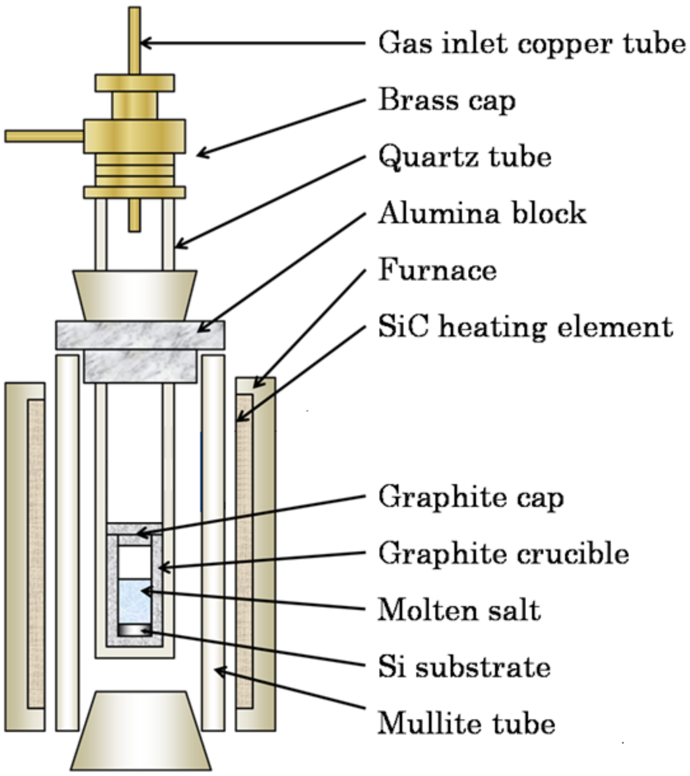
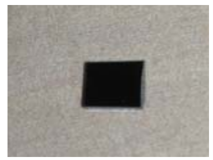


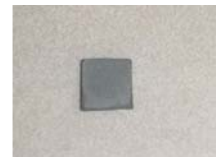
Fig. Schematic image of apparatus

Formation of β-$FeSi_2$ on Si wafer

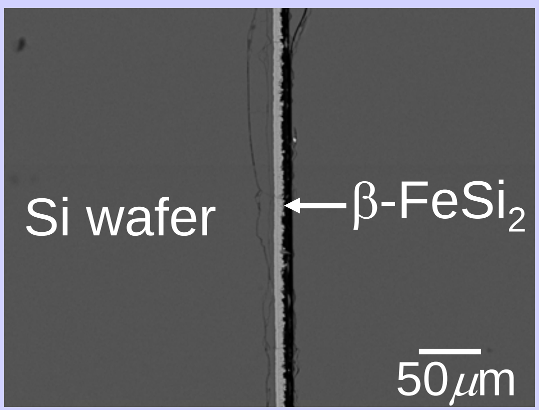
Reaction time :5 hours
$FeCl_2$ concentration in molten salts :0.02 at%



Si wafer



Treated sample



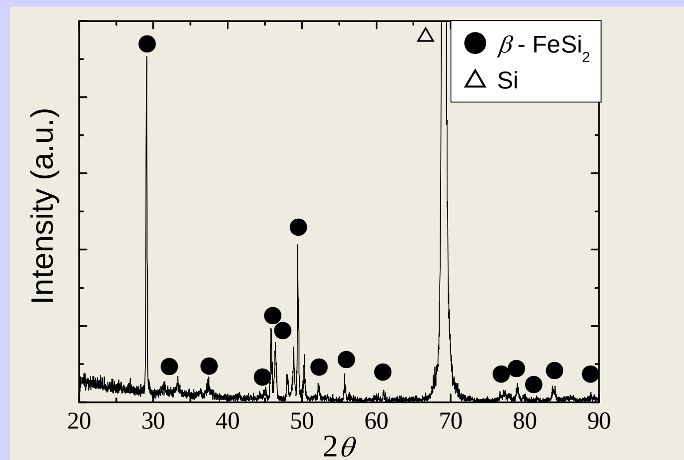


Fig. Cross-sectional SEM (up) image and XRD pattern (bottom) of the sample.

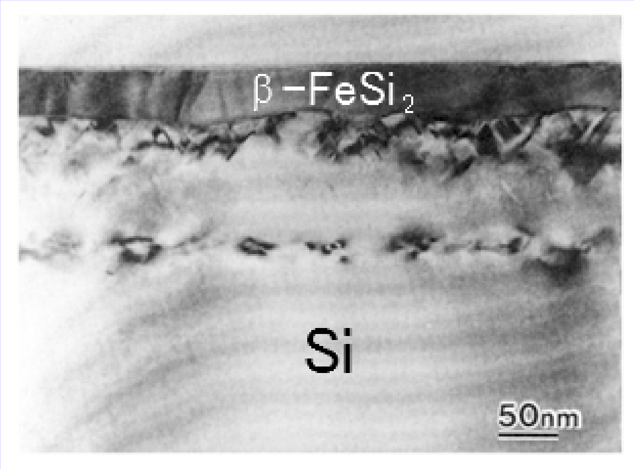
Confirmation of formation of β-$FeSi_2$ on Si wafer

Comparison with other methods

Reaction time :5 hours
$FeCl_2$ concentration in molten salts :0.02 at%

IBS method

This work



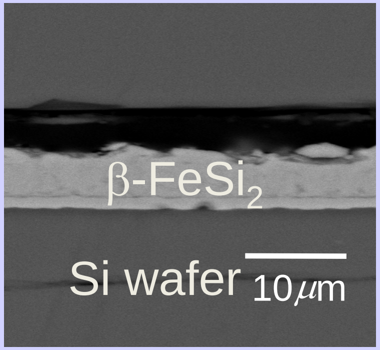


Fig. SEM images of samples prepared by IBS (left) and this work (right)

Thicker layers were obtained by higher deposition rates

Effect of the $FeCl_2$ Concentration

Reaction time : 5 hours

$FeCl_2$ = 0.02 at%　　$FeCl_2$ = 0.10at%　　$FeCl_2$ = 5.0 at%

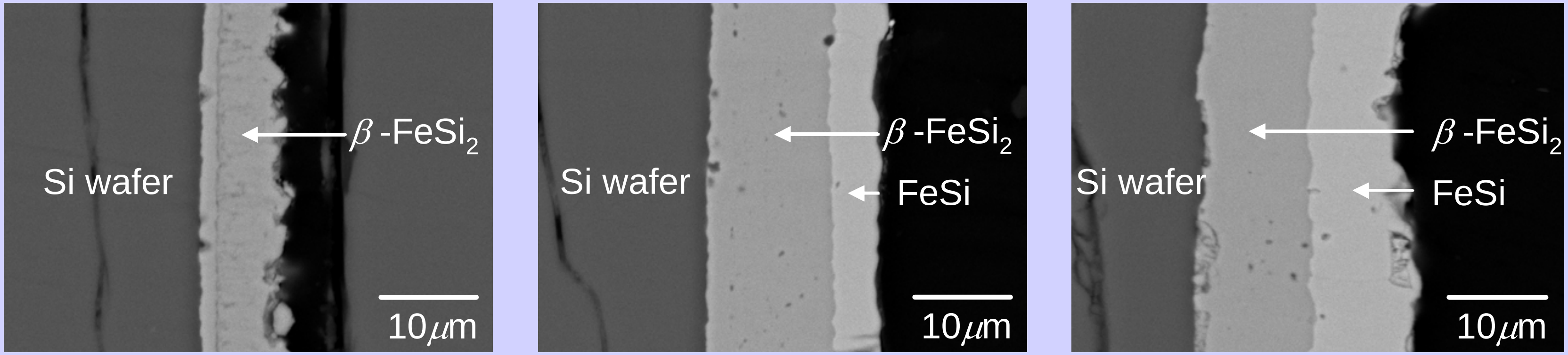


Fig. Cross-sectional SEM images of samples

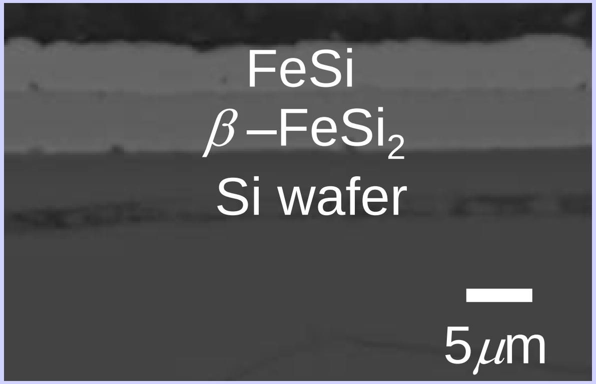
FeSi and β-$FeSi_2$ layers are formed by changing $FeCl_2$ concentration in molten salts

Single β-$FeSi_2$ layer formed by annealing to relax the difference of chemical potential between FeSi and β-$FeSi_2$?

Effect of annealing 1

Before

Reaction time :1 hour
$FeCl_2$ concentration in molten salts :1.0 at%



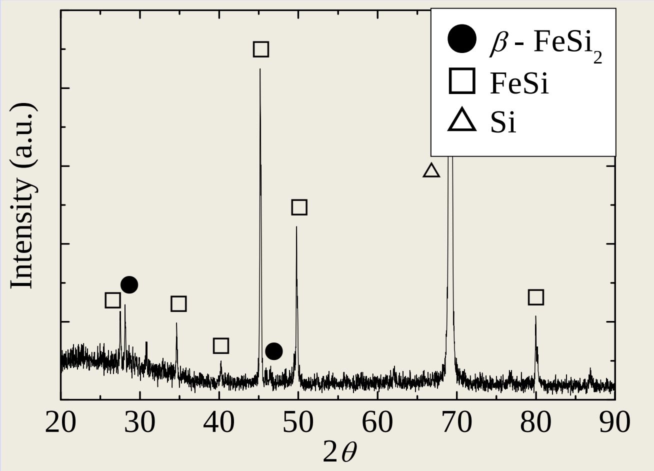


Fig. Cross-sectional SEM images (left) and XRD pattern (right) of samples

Effect of annealing 2

After

Annealing for 12hours

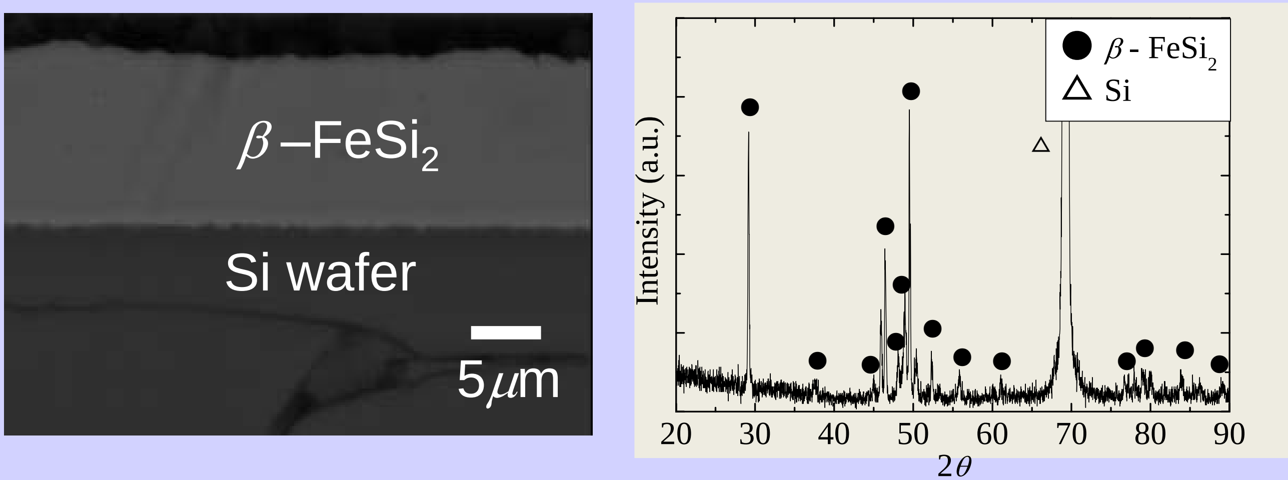


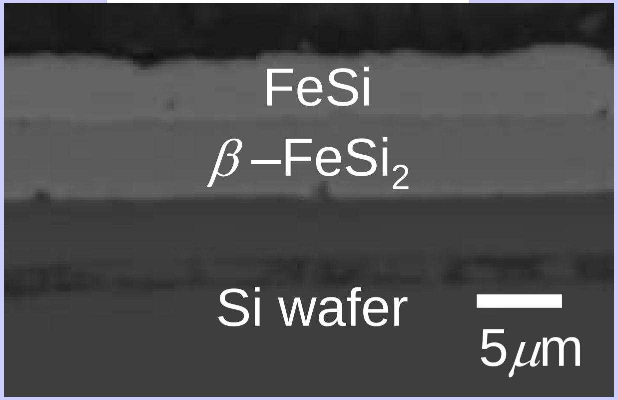
Fig. Cross-sectional SEM images (left) and XRD pattern (right) of samples

Formation of β-$FeSi_2$ single layer by annealing

Effect of crystal orientation

Reaction time :1 hour
$FeCl_2$ concentration in molten salts :1.0 at%

(a) Si(100)



(b) Si(110)

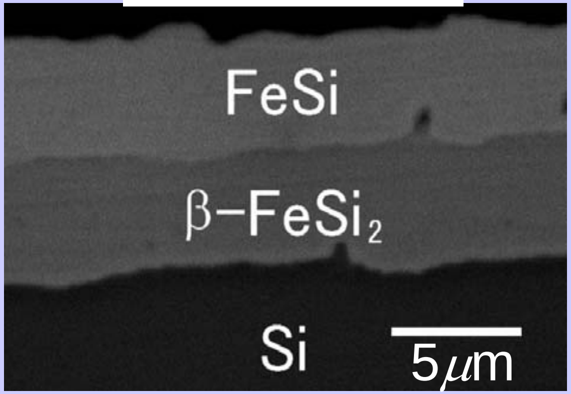


Fig. Cross-sectional SEM images of samples

FeSi and β-$FeSi_2$ layers also on the Si(110)

Conclusion

- Formation of β-$FeSi_2$ Films on Si(100) wafer was succeeded
- FeSi and β-$FeSi_2$ layers are formed by changing $FeCl_2$ concentration in Molten salts
- Formation of single β-$FeSi_2$ layer was achieved by annealing FeSi and β-$FeSi_2$ layers
- FeSi and β-$FeSi_2$ layers is formed also on the Si(110)
- Thicker layers were obtained by higher deposition rates

Future work

- Evaluation of optical and electric properties of the obtained β-$FeSi_2$
- Investigation of the reaction mechanism and development of the process